

# Off-Equilibrium Effective Temperature in Monatomic Lennard-Jones Glass

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The off-equilibrium dynamics of a monatomic Lennard-Jones glass is investigated after sudden isothermal density jumps (*crunch*) from well equilibrated liquid configurations towards the glassy state. The generalized fluctuation-dissipation relation has been studied and the temperature dependence of the violation factor  $m$  is found in agreement with the one step replica symmetry breaking scenario, i. e. at low temperature  $m(T)$  is found proportional to  $T$  up to an off-equilibrium effective temperature  $T_{\text{eff}}$ , where  $m(T_{\text{eff}})=1$ . We report  $T_{\text{eff}}$  as a function of the density and compare it with the glass transition temperatures  $T_g$  as determined by equilibrium calculations.

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In the last few years the off-equilibrium dynamics of glassy systems has been the object of intensive analytical and computational studies, due to the very rich phenomenology exhibited and the possibility to obtain detailed information on the phase-space properties of the glassy system itself. One of the most important features of the off-equilibrium regime is the generalization of the fluctuation-dissipation relation [1]. At equilibrium the Fluctuation-Dissipation Theorem (FDT) [2] states that the susceptibility,  $\chi_{AB}(t)$ , that describes the response of the variable  $A(t)$  to an external field conjugate to the variable  $B(t)$  is proportional, through the factor  $\beta=(K_B T)^{-1}$ , to the derivative of the cross correlation function of the variables  $A(t)$  and  $B(t)$  themselves,  $C_{AB}(t)$ . In the off-equilibrium case both susceptibilities and correlation functions are two-times quantities and the FDT no longer holds. However, as suggested by Cugliandolo and Kurchan through analytical studies of soluble spin glass models [3], the FDT can be generalized: the ratio between  $\chi_{AB}(t_1, t_2)$  and  $\beta \dot{C}_{AB}(t_1, t_2)$  defines a function,  $X(t_1, t_2)$ , that depends on the times  $t_1, t_2$  only through the actual value of the correlation function  $C_{AB}(t_1, t_2)$ ,  $X(t_1, t_2) \equiv X(C_{AB}(t_1, t_2))$ . The behavior of  $X(C_{AB})$  gives information on the equilibrium order parameter in the low temperature phase [3–5], in agreement with numerical experiments on spin glasses [6].

The conjecture of the similarity between structural glasses and some spin glass model [7] has been the basis to extend these analytical results on spin glasses to structural glasses. According to the latter conjecture one expects, in structural glasses, that  $X(C_{AB})$  is a two values function, with  $X(C_{AB})=1$  at short times and  $X(C_{AB})=m < 1$  in the non trivial long time region (the so called *aging* region). The constant  $m$  is expected to be proportional to the temperature of the system up to an effective temperature  $T_{\text{eff}}$ , above which  $m=1$  and, therefore, the FDT is recovered. In the numerical tests of this scenario performed so far [8], the system is brought off-equilibrium at constant density by sudden temperature jumps (*quench*), and the effective temperature  $T_{\text{eff}}$

is found to coincide with the glass transition temperature  $T_g$ . This is explained assuming that during the *quench* the system "captures" the properties of the  $3N$ -dimensional potential energy surface at that temperature where the relaxation time becomes comparable with the simulation time ( $T_g$ ) and, at lower  $T$ , it is no longer able to equilibrate. In this way the actual aging dynamics coincides with those at  $T_g$  even if the "true" temperature is  $T < T_g$ . This is a reasonable scenario, but it is still unclear what happens if the system is brought out of equilibrium without crossing the thermodynamic state  $(T_g, \rho)$ .

In this Letter we numerically investigate the off-equilibrium fluctuation-dissipation relation in a simple monoatomic glass, whose particles interacts via a Lennard-Jones (LJ) potential modified in such a way to avoid the crystallization occurring in standard LJ. At variance with the usual constant density temperature jumps method (*quench*), we use density jumps at constant temperature (*crunch*) in order to produce off-equilibrium configurations. As expected, at low temperature, we find violation of the equilibrium FDT in agreement with previous computational results in other model glasses [8]. We also find a linear temperature dependence of the off-equilibrium parameter  $m$  in the aging region, thus confirming the conjecture of one step replica symmetry breaking scenario for real glasses [7]. More important, the effective temperature  $T_{\text{eff}}$ , below which  $m < 1$ , is found very close to the glass transition temperature  $T_g$  at the density reached after the jump. While in the usual *quench* from high  $T$  at constant  $\rho$  it seems natural to visualize the process of freezing at  $T_g$  during the quench, in our *crunch* method the identification of the two temperature  $T_{\text{eff}}$  and  $T_g$  evidences how the effective temperature depends only on the density of the final state and does not depends neither on the initial state nor on the path in  $(T, \rho)$  plane. This observation gives a strong support to the idea that the aging process can be considered as a pathway in the  $3N$ -d energy landscape from the off-equilibrium situation towards the glassy minima [9].

The investigated system is a Modified Lennard-Jones

(MLJ) model glass, with  $N=256$  particles. The potential energy is  $V=V_{LJ}+\delta V$ , where  $V_{LJ}$  is the usual 6-12 Lennard-Jones interaction (in the following all the dimensional quantities are expressed in reduced units) and  $\delta V$  is a many-body term that inhibits crystallization:

$$\delta V = \alpha \Sigma_{\vec{q}} \theta(S(\vec{q}) - S_0) [S(\vec{q}) - S_0]^2. \quad (1)$$

Here  $S(\vec{q})$  is the static structure factor and the parameters in  $\delta V$  ( $\alpha^*=0.8$  and  $S_0=10$ ) have been tuned in order to avoid crystallization without introducing a perturbation on the "true" LJ dynamics [10]. The sum is made over all  $\vec{q}$  with  $q_{max}-\Delta < |\vec{q}| < q_{max}+\Delta$ , where  $q_{max}^*=7.12(\rho^*)^{1/3}$  and  $\Delta^*=0.34$ . With this potential we can investigate all the phase space without falling down in spatially ordered configurations and with negligible corrections to the equation of state of monatomic LJ.

First we study equilibrium properties of the system, determining the liquid-glass transition line in the  $(T, \rho)$  plane. The system is equilibrated at high temperature at different densities, from  $\rho^*=0.87$  to  $\rho^*=1.21$ , then it is slowly cooled ( $dT^*/dt^*=4.2 \cdot 10^{-4}$ ) measuring the potential energy as a function of  $T$ .

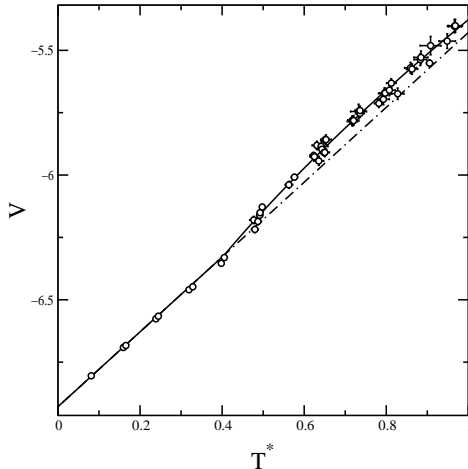


FIG. 1. Potential energy vs temperature (all in LJ units) during the cooling process from high temperature. The open circles are the molecular dynamics data, the solid line is the fitted curve (see text) and the dashed line is the harmonic extrapolation at high temperatures.

In Fig. 1 we report an example of the potential energy vs  $T^*$  at density  $\rho^*=0.99$ . It is evident the existence of a temperature  $T_g^*$  that marks the transition between two smooth regimes: at high  $T$ , in the liquid, as conjecture by Rosenfeld and Tarazona [11] the potential energy follows a  $T^{3/5}$  law while at low  $T$ , in the glass, the linear behaviour expected for harmonic glasses is recovered. In this way we are able to reconstruct the liquid-glass transition line  $T_g^*(\rho^*)$ , as reported in Fig. 2. Below  $\rho^*=0.87$  a spinodal decomposition takes place, evidenced by the appearance of "bubbles" in the sample.

We focus now on the fluctuation-dissipation relation. This relation connects the correlation function to the response to an external field. Let be  $A(t)$  and  $B(t)$  two generic microscopic quantities, and  $\Delta\mathcal{H}=\lambda h(t)B(t)$  a perturbation added to the Hamiltonian, with  $h(t)=0$  for  $t < t_w$  and  $\lambda$  an adimensional control parameter. If we define the correlation function at zero perturbation,  $C_{AB}(t, t_w)$ , as:

$$C_{AB}(t, t_w) = \langle A(t)B(t_w) \rangle_{\lambda=0}, \quad (2)$$

and the corresponding response function  $\chi_{AB}$ :

$$\chi_{AB}(t, t_w) = \lim_{\lambda \rightarrow 0} \frac{1}{\lambda} \frac{\delta \langle A(t) \rangle_{\lambda}}{\delta h(t_w)}, \quad (3)$$

(hereafter the subscript  $\lambda$  indicates that the average is performed in presence of the perturbing term in the Hamiltonian) then the equilibrium fluctuation-dissipation relation takes the form:

$$\chi_{AB}(t, t_w) = -\beta \partial C_{AB}(t, t_w) / \partial t_w. \quad (4)$$

We notice that even if at equilibrium the presence of  $t_w$  is redundant, as  $\chi_{AB}(t, t_w)$  and  $C_{AB}(t, t_w)$  depend only on  $t - t_w$ , we choose to use a two times formalism in order to easily generalize the above formulas to off-equilibrium case.

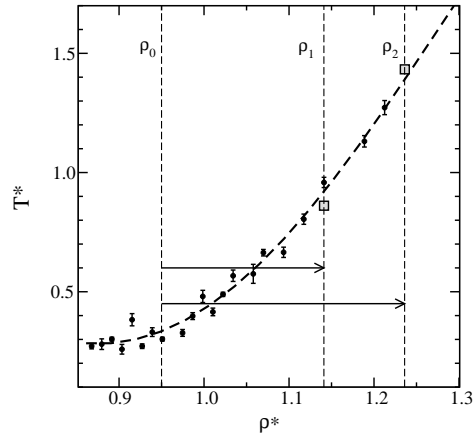


FIG. 2. The liquid-glass transition line in the plane  $(T^*, \rho^*)$  in reduced units. The black points are determined from crossover in the temperature dependence of equilibrium potential energy (the dashed line is a eyes guide). The two grey squares are off-equilibrium effective temperatures  $T_{eff}$  determined from fluctuation-dissipation relation. Arrows qualitatively describe the *crunch* process in the off-equilibrium analysis (from  $\rho_0^*=0.95$  to  $\rho_1^*=1.14$  and to  $\rho_2^*=1.24$ ).

Introducing the integrated response function  $R_{AB}(t, t_w)$ ,

$$R_{AB}(t, t_w) = \int_{t_w}^t dt' \chi_{AB}(t, t'), \quad (5)$$

we obtain from eq. (4) the fluctuation-dissipation relation in the integrated form:

$$R_{AB}(t, t_w) = \beta [C_{AB}(t, t_w) - C_{AB}(t, t)] . \quad (6)$$

In the present work we use the quantities  $A(t)$  and  $B(t)$ :

$$A(t) = \sqrt{2} (qN)^{-1} \sum_i \sin(\vec{q}_i \cdot \vec{r}_i(t) + \phi_i) , \quad (7)$$

$$B(t) = -\sqrt{2} q^{-1} \sum_i \sin(\vec{q}_i \cdot \vec{r}_i(t) + \phi_i) , \quad (8)$$

where  $\phi_i$  is a uniform random phase,  $\vec{q}_i = q\vec{s}_i$ ,  $\vec{s}_i$  a vector whose Cartesian components are random variables  $\pm 1$ , and  $q=2\pi n/L$ , with  $n$  an integer and  $L$  the sample size. Moreover we choose  $h(t) = h_o \theta(t - t_w)$  ( $h_o^*=1$  hereafter). From Eq. (2), after an average over the random phases  $\phi_i$ , one gets:

$$C_{AB}(t, t_w) = -(q^2 N)^{-1} \sum_i \langle \cos(\vec{q}_i \cdot \delta \vec{r}_i(t, t_w)) \rangle_{\lambda=0} , \quad (9)$$

where  $\delta \vec{r}_i(t, t_w) = \vec{r}_i(t) - \vec{r}_i(t_w)$ , and, according to Eqs. (3) and (5),

$$R_{AB}(t, t_w) = \sqrt{2} (q\lambda N)^{-1} \sum_i [ \langle \sin(\vec{q}_i \cdot \vec{r}_i(t) + \phi_i) \rangle_{\lambda} + \langle \sin(\vec{q}_i \cdot \vec{r}_i(t_w) + \phi_i) \rangle_{\lambda=0} ] . \quad (10)$$

(Fortunately in the limit  $N \rightarrow \infty$  the r.h.s of the equations becomes self-averaging). A more suitable and easy to compute form is obtained in the limit  $\vec{q}_i \cdot \delta \vec{r}_i \ll 1$ . In this limit, and averaging over  $\vec{s}_i$ , Eq. (9) becomes:

$$C_{AB}(t, t_w) \simeq -q^{-2} + \Delta(t, t_w)/2 , \quad (11)$$

having defined the mean square displacement:

$$\Delta(t, t_w) = N^{-1} \sum_i \langle |\vec{r}_i(t) - \vec{r}_i(t_w)|^2 \rangle_{\lambda=0} . \quad (12)$$

Similarly, Eq. (10) becomes:

$$R_{AB}(t, t_w) \simeq (\lambda N)^{-1} \sum_i [ \langle \vec{f}_i \cdot \vec{r}_i(t) \rangle_{\lambda} - \langle \vec{f}_i \cdot \vec{r}_i(t_w) \rangle_{\lambda=0} ] \quad (13)$$

where we have introduced the force  $\lambda \vec{f}_i$  acting on the particle  $i$  due to the perturbation term in the Hamiltonian:

$$\vec{f}_i = \sqrt{2} \vec{s}_i \cos(\vec{q}_i \cdot \vec{r}_i(t_w) + \phi_i) , \quad (14)$$

this is a random variable due to the randomness of  $\phi_i$  and  $\vec{s}_i$ . Therefore, from Eqs. (11,13), Eq. (6) becomes

$$2 R(t, t_w) = \beta \Delta(t, t_w) . \quad (15)$$

In the off-equilibrium case one can always define a violation factor  $X(t, t_w)$  in such a way to rewrite the Eq. (4) as follows:

$$\chi_{AB}(t, t_w) = -\beta X_{AB}(t, t_w) \partial C_{AB}(t, t_w) / \partial t_w . \quad (16)$$

In some recent papers [3] it has been conjectured that, in the aging region,  $X_{AB}(t, t_w)$  depends on its arguments only through the correlation function  $C_{AB}(t, t_w)$ . This allows to generalize the fluctuation dissipation relation (6) as:

$$R(C_{AB}) = -\beta \int_{C_{AB}(t, t_w)}^{C_{AB}(t, t)} dC_{AB} X(C_{AB}) , \quad (17)$$

or

$$dR(C_{AB})/dC_{AB} = \beta X(C_{AB}) . \quad (18)$$

In our specific case we obtain:

$$2 dR(\Delta)/d\Delta = \beta X(\Delta) , \quad (19)$$

which generalizes Eq. (15). In this work we have studied the generalized FDT, in the form expressed by Eq. (19). For sake of simplicity rather than perturbing the system with the random force  $\vec{f}_i$  in Eq. (14), we have used a random force  $\vec{f}'_i$  with the same variance of  $\vec{f}_i$  ( $\langle f^2 \rangle = 1$ ) and Cartesian components  $\pm 1$  with equal probability. Equation (15) has been numerically tested at equilibrium (see the upper part of Fig. 3).

The off-equilibrium states are obtained by *crunches* from an initial equilibrated configuration at density  $\rho_0^*=0.95$  at a given temperature  $T$  to a final state at the same  $T$  and higher density ( $\rho_1^*=1.14$  and  $\rho_2^*=1.24$ ). We set the time of the *crunch* as  $t=0$ . For each investigated  $T$  and  $\rho$  we perform an isothermal molecular dynamics simulations with  $\lambda=0$  and calculate  $\Delta(t, t_w)$  as a function of  $t$  and  $t_w$ . Starting from the same  $t=0$  configurations, after a waiting time  $t_w$  we switch on the external field ( $\lambda \neq 0$ ) and measure the response  $R(t, t_w)$ . The strength of the external field  $\lambda^*=0.27$  was chosen after extensive tests of the linear dependence of the response on the perturbation. All the measured quantities are averaged over 50 initial configurations and 10 random extractions of the variables  $\vec{f}'_i$ . The  $t_w$  values investigated are  $t_w^*=1, 5, 10$ . As an example, in Fig. 3 we show the quantities  $\Delta$  and  $2R/\beta$  after a *crunch* from  $\rho_0^*=0.95$  to  $\rho_2^*=1.24$  for three different temperatures,  $T^*=1.76, 0.96, 0.48$ , and for  $t_w^*=5$ . In the left hand part the two quantities are plotted versus  $\log(t/t_w)$  while in the right side  $2R/\beta$  is plotted as a function of  $\Delta$ . All the data are compatible with the assumption that violation factor  $X$  depends on  $t$  and  $t_w$  only through  $\Delta(t, t_w)$ , as verified comparing the results obtained for different values of the waiting time. Moreover the measured values  $X(\Delta)$  are well represented by a piecewise constant behavior ( $X=1$  for short times and  $X<1$  at longer times) suggesting a one step replica symmetry breaking scenario for structural glasses as conjectured in [7] and already found in [8] in the cases of quenching systems of soft spheres and LJ binary mixture.

In Fig. 4 we show the  $T$  dependence of the violation factor  $m(T)$  in the aging region, for the two final densities analyzed. It is evident a linear behavior up to a temperature  $T_{eff}$ , as found at low temperature in all know cases in which one step replica symmetry holds. Fitting the data with the expression  $m(T)=aT\theta(T_{eff}-T)+\theta(T-T_{eff})$  we extract the corresponding  $T_{eff}$  values, which turn out to

correspond with the previously measured equilibrium values of  $T_g$  as evidenced Fig. 1. The coincidence between  $T_{eff}$  at a given final density and  $T_g$  at the same equilibrium density evidences supports the hypothesis that, in the aging region, the point representing the system in the  $3N$ -d energy landscape moves from the region pertaining to "high temperatures", where it has been brought by the sudden density change, towards those configurations where the characteristic time for structural rearrangement "diverges" [9].

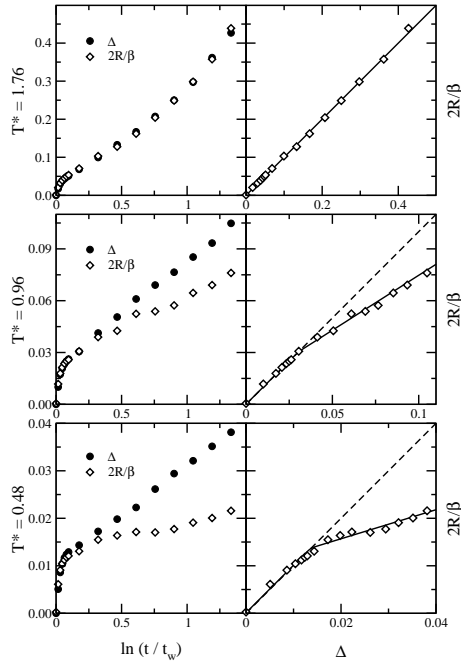


FIG. 3. Mean square displacement  $\Delta$  and integrated response function  $2R/\beta$  in reduced units at  $\rho_2^*=1.24$  for three temperatures  $T^*=0.48, 0.96, 1.76$ . The left side shows the log time dependence of the two quantities. In the right side the response function vs  $\Delta$ . Dashed lines indicate equilibrium fluctuation-dissipation relation, while full lines fit the off-equilibrium aging region.

In conclusion we have, for the first time, studied the off equilibrium dynamics of a simple monatomic glassy system: a LJ potential where the crystallization has been inhibited adding a small many-body term. The system has been brought off-equilibrium via isothermal density jumps and the generalized fluctuation-dissipation relation has been studied. The found piecewise constant behavior of the the violation factor and its linear temperature dependence agrees with one step replica symmetry scenario conjectured for structural glasses. For a given density, the emergent off-equilibrium effective temperature  $T_{eff}$  seems to be very close the glass transition temperature  $T_g$ , determined by equilibrium molecular dynamics measures. Then, even if brought out of equilibrium by *crunches* at constant  $T$  at final density  $\rho$  without crossing the  $T_g(\rho)$  transition point, the system captures the properties of energy surface at  $T_{eff} \sim T_g(\rho)$ .

The off-equilibrium effective temperature  $T_{eff}$  is then independent on the particular path in  $(T, \rho)$  plane crossing the transition line, and depends only on the final reached density.

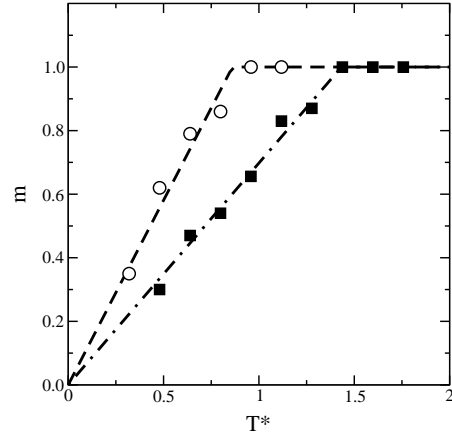


FIG. 4. Temperature dependence of the violation factor in the off-equilibrium aging region for two densities:  $\rho_1^*=1.14$  (open circles) and  $\rho_2^*=1.24$  (full squares). From the fits (dashed lines) one obtains:  $T_{eff}(\rho_1^*)=0.86$  and  $T_{eff}(\rho_2^*)=1.43$ .

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